

LIQUID-PHASE CRACKING OF POLYVINYL CHLORIDE (PVC) ROLE OF SOLVENT ON DECOMPOSITION OF PVC AND REMOVAL OF CHLORINE

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INTRODUCTION

Development of feed stock recycling of waste plastics is very important not only for minimization impact for environment but also for saving energy resources. In past two decades, incineration or conventional decomposition of the waste plastic have been studying mainly. However, incineration caused damages in furnace and air pollution problem. Quality of the oil from the conventional decomposition was not enough for fuel or feeds to chemical industry. On the other hand, no hazard byproducts, higher quality oil, lower yields of gas and residue can be expected for liquid-phase cracking of the waste plastic, because products are hydrogenated by solvents and solvents prevent point heating cause coking reaction. We have been studying liquid-phase cracking of used tire (1), polystyrene, and polyethylene in various solvents. Interesting interactions between solvents and plastics were observed (2).

PVC have been used widely as well as other three major plastic, polyethylene, polypropylene, and polystyrene. However, due to high chlorine content and condensation of dechlorinated intermediate product, PVC is one of the most difficult plastics for feed stock recycling. Recently, Y. Maezawa et al. reported PVC was converted into oil at 600 °C with sodium hydroxide (3). However, more than 50 % of hydrocarbon fraction of PVC was converted to residue and gas. In our previous study, we showed advantage of liquid-phase cracking of PVC (4). However, maximum yield oil was only 50 % even at 470 °C under 6.9 MPa of hydrogen, because dechlorinated PVC, heated at 300 °C for three days, was used. In this work, PVC was converted into liquid products directly in tetralin or decalin at 440 °C by using an autoclave specially treated for corrosion by chloride.

EXPERIMENTAL

Reaction procedure: PVC resin (24.0 g) and tetralin or decalin (50.0 g) were charged into a 200 ml magnetic stirred autoclave made of hastelloy C. The most of experiments were carried out at 440 °C for 60 min under an initial pressure of 4.0 MPa of nitrogen gas. In this paper, 0 min of reaction time, shown in figures and table, means that reactor was quenched just after temperature reached 440 °C. In some experiments, copper powder (6 g) or sodium hydroxide (15.6g) was added. In order to study effects of pretreatment of PVC, two kinds of dechlorinated PVC, DeCl-1 and DeCl-2, were used. The DeCl-1 was produced from PVC by heating at 300 °C for 12 hours under nitrogen gas. The DeCl-2 was prepared from the products of PVC heated in tetralin at 440 °C for 0 min. In a few experiments, reaction was carried out at 440 °C for 60 min under 10 MPa with nitrogen gas flowing. Reaction products were separated gas, oil, vacuum bottom, and residues by filtration and vacuum distillation. The oil was defined distilled liquid products at 330 °C for 60 min under vacuum. The vacuum bottoms were separated HS (hexane soluble) and HI (hexane insoluble) by soxhlet extraction for more than two days. The HS, HI, and residue were dried for one day at 110 °C under vacuum and weighted.

Analysis of products: Gas products were collected into a Teflon bag through two gas washers filled with water and analyzed by gas chromatography (GASUKURO KOGYO, GC-312, molecular sieve 5A, molecular sieve 13X, Porapak N, gasukuro 54, and VZ-7). Liquid products were analyzed by gas chromatography (CARLO ERBA INSTRUMENTS, HRGC 5300) with capillary column (HP Ultra-1, 0.2 mm, 50m). Each compound in liquid product was identified by GC-MS (Hewlett Packard 5973) with capillary column of HP Ultra-1. Chlorine compounds were identified by GC-MS and GC with atomic emission detector (AED, Hewlett Packard 5921). Chlorohexane and chloronaphthalene were used as an internal standard for quantitative measurement.

RESULTS AND DISCUSSION

Effect of solvent on distribution of products: Distributions of the products from the PVC resin were shown in Fig. 1. Yields of oil, residue in tetralin and decalin for 0 min of reaction time were 39 %, 2.4 % and 73 %, 14% respectively. In our previous experiment, yields of oil and residue from the dechlorinated PVC were 8 %, 13 % for 60 min. The significantly higher yield of oil in decalin indicated that direct liquid-phase cracking of PVC was an effective process and PVC was decomposed in a short time while reactor was heated up to 440 °C. On the other hand, lower yields of oil and residue in tetralin implied that decomposition of PVC to oil and condensation to residue was retarded in tetralin. The effect of tetralin might be caused by quick stabilization of radicals by hydrogen from tetralin. The

similar suppressing effect of tetralin was observed in the liquid phase cracking of polyethylene and polystyrene at relatively low temperature. The oil yield in tetralin increased with reaction time. On the other hand, slight increase of oil yield was observed in decalin. These results showed that hydrogen from tetralin enhanced conversion of HS and HI to oil at 440 °C.

Identified compounds in oil from PVC were shown in Table 1. Benzene, toluene, and other alkyl benzene were observed in both solvents. As trace products, anthracene, diphenyl methane, and triphenyl were detected. Characteristic compounds, alkyl tetralin, alkyl naphthalene, tetralin dimmer, and naphthalene dimmer, were produced in tetralin. Almost same yields of benzene, toluene, and alkyl benzene in both solvents implied that these compounds were produced from PVC directly not from tetralin. Particularly, benzene was considered to be produced during heating time, because more than 6 % of benzene was produced for 0 min

Effect of solvent on distribution of chlorine compounds: Lower chlorine contents of products is very important for fuel and feed stock recycling of waste plastics. However, it is difficult to identify each chlorine compound. In this work, we identified main chlorine compounds from PVC by using gas chromatography with atomic emission (AED). Spectrums of chlorine compounds were shown in Fig. 2. Main chlorine compounds from liquid-phase cracking of PVC in tetralin were hydrogen chloride, dichlorobutane, and chlorotetralin. Chlorine contents of the two organic compounds, dichlorobutane and chlorotetralin, were 229 ppm, 171 ppm for 0 min and 14 ppm, 28 ppm for 60 min respectively. When decalin was used as solvent, main chlorine products were hydrogen chloride, dichlorobutane, and chlorodecalin. Chlorine contents of main organic chlorine compounds from liquid phase cracking of PVC were shown in Fig. 3. Total chlorine contents of oil for 0 min and 60 min were 624 ppm, 50 ppm in tetralin and 4040 ppm, 1746 ppm in decalin respectively. These results showed that tetralin was very effective solvent to reduce chlorine contents.

In order to remove chlorine in oil from PVC, sodium oxide have been used in many past experiments. Recently, copper was pointed out to be the catalyst for production of dioxin under incineration (5). Effects of addition of these compounds and pretreatment of PVC on chlorine contents in oil were shown in Fig. 4. In the presence of sodium hydroxide, slight of hydrogen chloride was produced in the gas products, because most of chlorine was converted to sodium chloride. However, total chlorine content of organic chlorine compounds was almost same as that without sodium hydroxide. On the other hand, remarkable increase of dichlorobutane was observed in oil from liquid-phase cracking of PVC with copper powder.

The higher chlorine contents in oil from DeCl-1 and DeCl-2 implied that dechlorination of PVC by heating under nitrogen gas or in tetralin was not effective pretreatment to reduce chlorine in oil. The difficulty of removal of chlorine may be caused by structure of pretreated PVC. The lowest chlorine contents of oil was observed in direct liquid-phase cracking with nitrogen gas flowing.

CONCLUSION

More than 70 % of oil yield was obtained on direct liquid-phase cracking of PVC at 440 °C under nitrogen gas. Particularly, tetralin was effective not only for increase of oil but also for reduction of total chlorine contents in the oil. Benzene was produced from PVC directly. Hydrogen chloride, dichlorobutane, chlorotetralin, and chlorodecalin were main chlorine compounds in oil from PVC. Dichlorobutane increased significantly in the presence of copper. Sodium oxide removed hydrogen chloride perfectly. However, it was not effective to reduce organic chlorine compounds in oil.

PVC was converted to oil contained low chlorine at higher yield by direct liquid-phase cracking. The process was expected to be effective for feed stock recycling of PVC and waste plastics.

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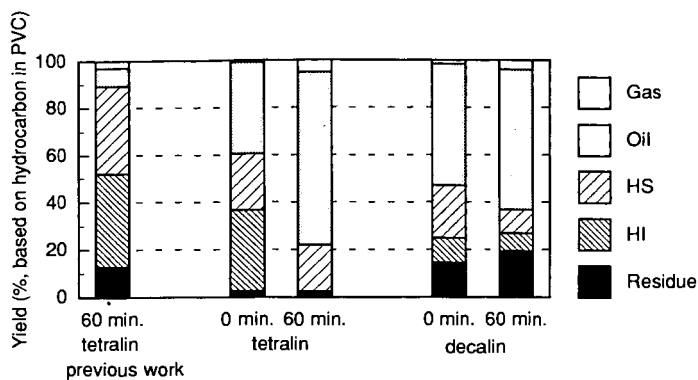


Fig. 1 Distribution of products from PVC at 440 °C

Table 1 Liquid products from PVC at 440C

(%, based on hydrocarbon in PVC)

solvent	tetralin	tetralin	decalin	decalin
reaction time	0 min	60 min	0 min	60 min
hydrocarbon in PVC	100.0	100.0	100.0	100.0
solvent	482.2	482.2	482.2	482.2
benzene	6.7	8.9	7.4	9.0
toluene	0.6	3.6	0.8	1.5
C2,C3-benzene	1.0	4.1	1.1	3.6
C4-benzene	1.8	14.8	0.8	4.7
decalin	0.0	0.0	490.1	459.4
1-methylindane*	3.4	36.8	0.0	0.0
tetralin*	464.3	332.3	7.0	11.9
naphthalene*	26.6	92.5	1.3	4.8
Alkyl-tetralin*	0.7	2.3	0.3	0.4
Alkyl-naphthalene*	0.6	3.0	0.4	0.9
diphenylmethane	0.2	0.7	0.3	0.5
anthracene	0.2	0.5	0.2	0.3
tetralin dimmer*	2.5	5.0	0.0	0.2
naphthalene dimmer*	0.3	1.6	0.1	0.2
total	508.9	506.2	509.8	497.4

*: products from solvent mainly

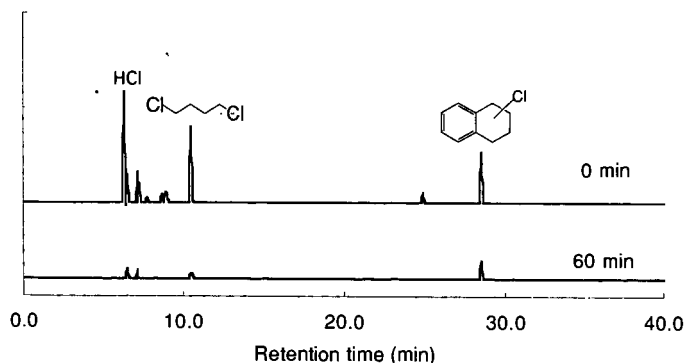


Fig. 2 Chlorine compounds in oil produced from PVC in tetralin at 440 °C

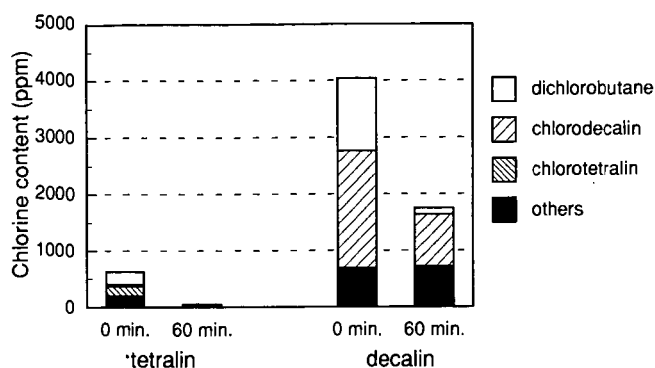


Fig. 3 Chlorine content of oil from PVC at 440 °C

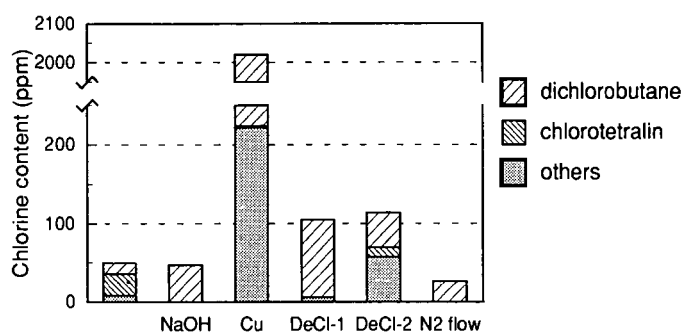


Fig. 4 Effect of additives and reaction procedures on chlorine content in oil from PVC at 440 °C